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We report a detailed quantum-chemical investigation of donor-acceptor substituted dipolar nonlinear optical chromophores incorporating the 4-(dimethylamino)phenyl donor end group and a variety of strong heterocyclic acceptor end groups, including tricyanofurans and tricyanopyrroles. In particular, we study the variation of the molecular second-order polarizability (β) with the acceptor end group and when inserting auxiliary donors (thiophene) and acceptors (thiazole) into the π bridge. Both finite-field calculations (in the context of local contributions) and sum-over-states calculations were carried out in order to probe the relationship between β and the chemical structure of the various chromophores. The trends obtained with these two methods are fully consistent. The large β values (up to 700×10^{-30} esu) as well as the observed tunability of the optical absorption maximum (λ_{max}) make the chromophores investigated here interesting candidates for use in electro-optic applications at telecommunications wavelengths. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2155385]

I. INTRODUCTION

The second-order nonlinear optical (NLO) properties of conjugated organic molecules have been the focus of numerous experimental and theoretical investigations due to their utility in optoelectronics and photonics for applications including high-speed optical communications, integrated optics, and optical data processing and storage.[1] Bulk second-order NLO polarizabilities require noncentrosymmetric arrays of chromophores with high molecular second-order polarizabilities β. In order to obtain high β, conjugated organic molecules are typically substituted with electron-donor and electron-acceptor end groups; the required bulk noncentrosymmetry is generally achieved using an electric-field poling of these chromophores above the glass-transition temperature (Tg) of a polymer host, and is then frozen in by cooling below Tg.[2] An understanding at the molecular level of the relationships between chemical structure, dipole moment, and NLO properties can provide a useful insight for the design of a new generation of chromophores.

It has been well established that the molecular second-order polarizability (or first hyperpolarizability) β depends on the strength of the donor and acceptor end groups and on the nature and length of the π bridge.[3] In addition, it is important to keep in mind that for most practical applications large polarizabilities need to be accompanied by optical transparency in the wavelength range of interest. For instance, for telecommunications applications, it is important that the tail of the absorption peak does not extend significantly into the 1.30–1.55 μm range. This often requires a trade-off between chromophore optical nonlinearity and

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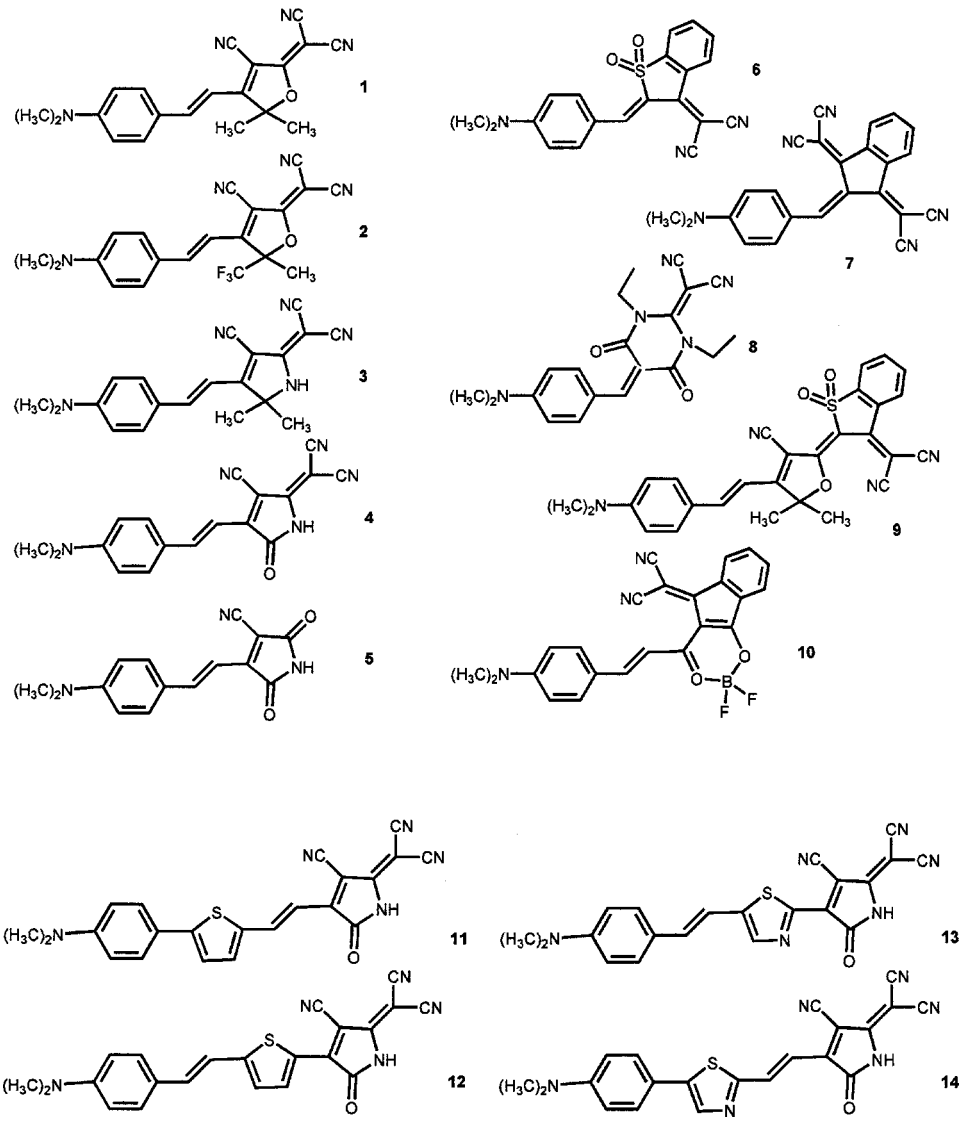

FIG. 1. Chemical structures of chromophores 1–14.

transparency, as for a given structure an increase in β due to an increase in acceptor end group strength is usually accompanied by a redshift of the optical-absorption maximum (λ_{max}). Ideally, new chromophores should show an increase in β along with a blueshift (or at least no significant redshift) of λ_{max} (Ref. 4) with regard to existing compounds, which is often difficult to achieve.

Recently, the 2-dicyanomethyl-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran acceptor end group, often referred to as "tricyanofuran" (TCF) (acceptor of chromophore 1, Fig. 1), has gained popularity as a strong acceptor end group suitable for incorporation into stable high β chromophores.[5] However, the role of the oxygen atom in the furan ring is still unclear,[6] and other related chemical structures may show more efficient molecular NLO properties. In the present contribution, the molecular second-order polarizability of a chromophore including a TCF acceptor end group (1) is compared to that of compounds including (i) the 2-dicyanomethyl-3-cyano-4,5-trimethyl-5-trifluoromethyl-2,5-dihydrofuran acceptor end group (acceptor of chromophore 2, Fig. 1), (ii) the pyrrole-based ["tricyanopyrrole" (TCP)] analogs of the TCF acceptor end group (acceptors of chromophores 3–5, Fig. 1), (iii) other previously studied strong acceptor end groups, such as 3-(dicyanomethylene)-2,3-dihydrobenzothiophene-1,1-dioxide (acceptor of chromophore 6, Fig. 1), 1,3-bis(dicyanomethylene)indane (acceptor of chromophore 7, Fig. 1), and 1,3-diethyl-2-dicyanomethylene-4,6-dioxohexahydro-pyrimidine (acceptor of chromophore 8, Fig. 1),[7] and (iv) two alternative heterocyclic strong acceptor end groups (acceptors of chromophores 9 and 10, Fig. 1).[8]

In addition, we have tested whether the concept suggested earlier[9] of inserting auxiliary donors and acceptors into the π bridge can be used to significantly enhance β and in which position these heterocycles are most effective. Therefore, in chromophores 11–14, an electron-rich ring (thiophene) or an electron-poor ring (thiazole) is inserted into the π bridge of chromophore 4, leading to four different types of structural motifs: D-D'-π-A (11), D-π-D'-A (12), D-π-A'-A (13), and D-A'-π-A (14).

II. METHODOLOGY

The geometries of the chromophores were optimized using the semiempirical Austin Model 1 (AM1) method[10] as implemented in the MOPAC 3.1 package. All molecules were

assumed to be in *anti configurations* (as shown in Fig. 1). In dipolar NLO chromophores, the molecular β is usually dominated by a single diagonal tensor term along the donor-acceptor axis. Accordingly, in this work, the x axis was defined as pointing from the central carbon of the dicyanovinylene unit of the acceptor end group in chromophores 1–5 and 11–14, and its equivalent position in chromophores 6–10 towards the nitrogen of the donor end group (with this choice, the x component of the dipole moment is positive). The β_{xxx} components defined in this way totally dominate the other tensor elements of β. Therefore, the discussion of the properties and trends of the molecular second-order polarizability will be limited to these β_{xxx} components.

On the basis of the AM1-optimized geometries, the electronic properties (state dipole moments, transition dipole moments, and transition energies) were evaluated from a semiempirical intermediate neglect of differential overlap (INDO) Hamiltonian.[11] The spectroscopic parametrization along with the Mataga-Nishimoto[12] electron repulsion scheme was used, as implemented in the ZINDO code. The INDO calculations were coupled to a single configuration interaction (SCI) scheme, which is known to give a reliable description of the properties of one-photon-allowed excited states, which are those involved in the perturbative description of the second-order polarizability (*vide infra*). The 30 highest occupied and 30 lowest unoccupied molecular orbitals were active in the SCI procedure, which is sufficient to reach converged β values in the compounds investigated here.

The second-order polarizabilities were calculated using the sum-over-states[13] (SOS) and finite-field (FF) approaches. The perturbative SOS method uses excitation energies, transition dipole moments, and state dipole moments obtained from the INDO/SCI calculations. In systems in which a single electronic excited state (e) is strongly coupled to the ground state (g), SOS results can be very efficiently analyzed in the framework of the two-state model[14] (comprising only the transition energy for excitation from (g) to (e), the associated transition dipole moment and the change in state dipole moment). In the chromophores investigated here, however, a large number of low-lying excited states (typically around four) contribute significantly to the SOS expression, preventing rapid convergence of the essential-state model. Consequently, in the present case, the SOS calculations mainly serve as a consistency check for the results and the analysis will be largely based on the FF approach, on the basis of the local contribution version,[15] as proposed by Chopra *et al.*[16] and developed by Nakano *et al.*[17] This method has been successfully applied to conjugated organic systems in conjunction with the INDO Hamiltonian.[18] Its particular advantage is that it allows one to discern the contributions of the individual chemical segments of the molecules to the overall β. The FF approach relies on the fact that, by definition, β_{xxx} is the second derivative of the x component of the dipole moment with respect to the x components of the applied electric fields (F) at zero field,

$$\mu_x(F_x) = \mu_x(0) + \alpha_{xx}F_x + \frac{1}{2!}\beta_{xxx}F_x^2 + \frac{1}{3!}\gamma_{xxxx}F_x^3 + \cdots, \tag{1}$$

where α, β, and γ are the molecular first-, second-, and third-order polarizabilities, respectively. The electronic part of β can be cast rigorously as the integral over the moments of the second derivative of the charge density ρ. In an approximate way, that integral can be partitioned into a sum over derivatives of point charges q_i concentrated on the individual atoms i,

$$\begin{aligned}\beta_{xxx} &= \left.\frac{\partial^2 \mu_x}{\partial F_x^2}\right|_{F_x=0} \\ &= \int x \left.\frac{\partial^2 \rho(\mathbf{r})}{\partial F_x^2}\right|_{F_x=0} d^3\mathbf{r} \\ &\approx \sum_i x_i \left.\frac{\partial^2 q_i^2}{\partial F_x^2}\right|_{F_x=0} = \sum_i x_i q_i^{(2)}.\end{aligned} \tag{2}$$

Here, β_{xxx} is partitioned into local (atomic) contributions or so-called β moments $x_i q_i^{(2)}$ derived from the so-called β charges $q_i^{(2)}$. Note that the superscript (2) represents the second derivative with respect to the applied electric field in the x direction (with the x subscript dropped to simplify the notation). In the calculations, the derivatives were approximated by finite differences obtained from INDO Hartree-Fock (HF) Mulliken charges, with fields of zero and $\pm 5.14 \times 10^{11}$ V/m (10^{-3} atomic units) applied to the chromophores; the series expansion for the charges was limited to the second order in F. These atomic β charges are then plotted in Figs. 2–4 as circles whose size corresponds to their values (in a common scale for all the molecules plotted) and shading to their signs (black for negative and white for positive).

Though the second-order polarizability, according to Eq. (2), is directly related to the moments of β charges $q_i^{(2)}x_i$, each moment is obviously dependent on the arbitrary choice of the axis origin, which can make plotting the moments somewhat misleading. Here, in order to display reliably the relative importance of the local contributions to β_{xxx}, the origin has been consistently chosen in the middle of the molecule (leading to opposite x signs at opposite ends). In this context, it is clear that an efficient chromophore should rather have large terminal contributions (where the moment arms are large), preferentially of the same sign for a given end, and of opposite signs at the opposite ends (to avoid cancellation of moments). As discussed below, many of the chromophores investigated here turn out to present such characteristics.

III. RESULTS AND DISCUSSION

The calculated transition energies, optical-absorption maxima, long-axis components of the second-order polarizability, and orientationally averaged second-order polarizabilities $\langle\beta\rangle$ are reported in Table I. For all compounds, the trends obtained for the average β values are fully reproduced

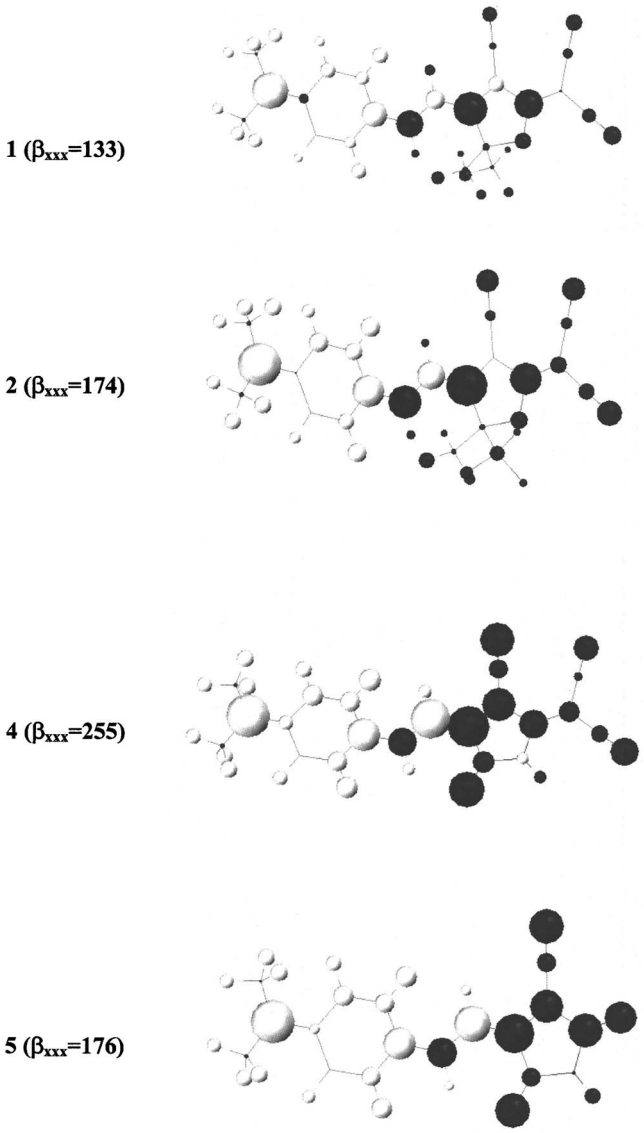

FIG. 2. Second derivatives of the atomic charges for chromophores 1, 2, 4, and 5. The circle size is proportional to the value of the β charge; the shading indicates their sign [the acceptor end groups display positive local contributions (black circles) and donor end groups display negative ones (white circles)]. The β_{xxx} FF values are also given in parentheses.

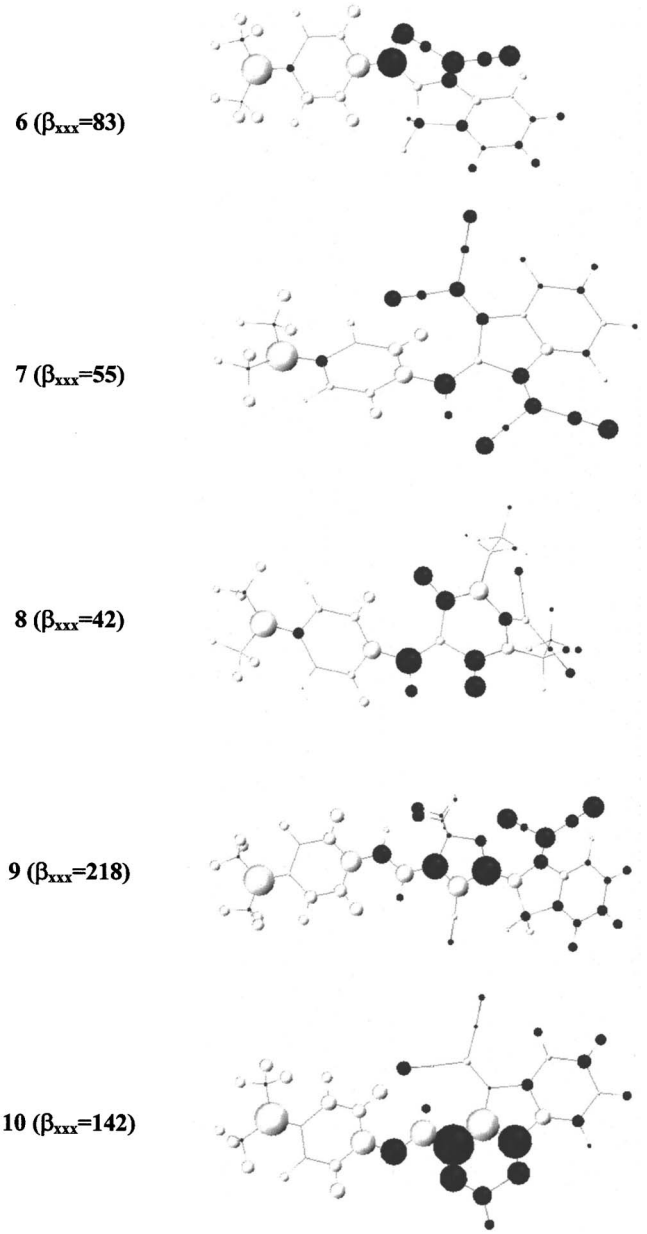

FIG. 3. Second derivatives of the atomic charges for chromophores 6–10 using the conventions of Fig. 2.

by β_{xxx} also, the trends and values obtained for the β_{xxx} components from the β charges and moments are consistent with those obtained with the SOS method.

A. Effect of varying the acceptor end group

For chromophore 1, we calculate a β_{xxx} component of 133×10^{-30} esu. This value increases by about 25% when one CH_3 group in the TCF acceptor end group is replaced by a CF_3 group [$\beta_{xxx}(2)=174\times10^{-30}$ esu]. This increase in β_{xxx} between 1 and 2 can be understood in terms of the inductive electron-withdrawing effect of the CF_3 group relative to that of the CH_3 group. A much larger change in the calculated β_{xxx} (increase by a factor of 2 compared to chromophore 1) is obtained for chromophore 4 [$\beta_{xxx}(4)=255\times10^{-30}$ esu]. To determine which of the structural modifications of the acceptor end group [(replacement of the furan by a pyrrole or substitution of the $C(CH_3)_2$ group with a carbonyl functional group)] is principally responsible for this increase, a chromophore based on another acceptor end group was investigated, in which only the oxygen is replaced by an NH (chromophore 3). The calculated β_{xxx}[$\beta_{xxx}(3)=117\times10^{-30}$ esu] did not change significantly compared to chromophore 1. Consequently, the replacement of the dimethylcarbon group by a carbonyl functional group appears to be the principal factor responsible for the large β_{xxx} component in chromophore 4. Although it has the highest β_{xxx} value among the systems discussed so far, chromophore 4 might not be very attractive when damping and transparency are an issue (as can be deduced from the 0.4 eV redshifted linear absorption maximum of 4 compared to 1). As expected, in chromophore 5, where one carbonyl replaces the dicyanovinylene unit of chromophore 4, β_{xxx} is some 25% lower than in 4 while remaining significantly larger than in 1.

To benchmark the effectiveness of the acceptor end

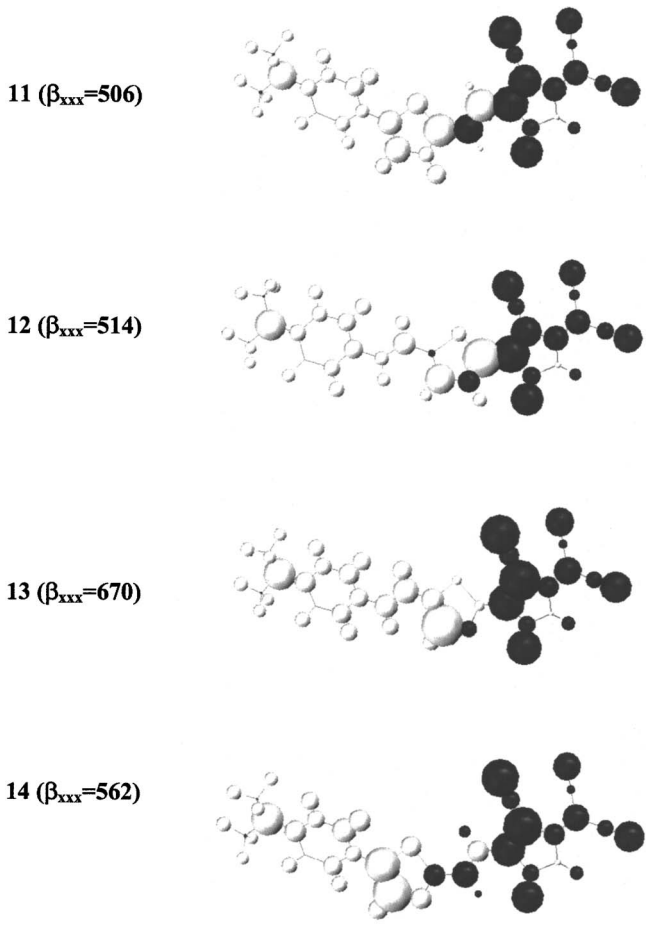

FIG. 4. Second derivatives of the atomic charges for chromophores 11–14 using the conventions of Fig. 2.

groups discussed above, they are compared to chromophores based upon the well-established 3-(dicyanomethylene)-2,3-dihydrobenzo-thiophene-1,1-dioxide (6), 1,3-bis(dicyanomethylene)indane (7), and 1,3-diethy1-2-dicyanomethylene-4,6-dioxohexahydropyrimidine (8) acceptor end groups.[7] In spite of their longer conjugation pathways, the β_{xxx} values calculated for 6–8 are significantly smaller than in chromophores 1–5, which underlines the high potential of TCF- and TCP-based acceptor end groups.

Finally, two alternative hypothetical acceptor designs were tested: chromophore 9, which can be regarded as the condensation product of the ketone precursor to the TCF acceptor with 3-(dicyanomethylene)-2, 3-dihydrobenzothiophene-1,1-dioxide and chromophore 10, where the acceptor end group is a hybrid of a 1,3,2-(2H)-dioxaborine with 1-(dicyanomethylene)indane. Dioxaborines are known to yield efficient acceptor end groups for NLO (Ref. 19) and electron-transport[20] applications. For systems 9 and 10, the calculated β_{xxx} values and transition energies are in the same range as for the TCF- and TCP-based chromophores 3, 4, and 5; the acceptor end groups and resulting molecular masses are, however, significantly larger than in the former systems.

In order to understand the molecular origin of the trends observed for β, we now turn to a discussion of the β charges obtained from FF calculations. The β charges are plotted for chromophores 1, 2, 4, and 5 in Fig. 2. The acceptor end groups display positive local contributions (black circles), while the donor end groups display negative contributions (white circles). We first observe that only variations in the magnitude of the β charges are observed in the dimethylamino donor end group and the phenylene segments, while the patterns remain qualitatively similar in all molecules. For all chromophores, the nitrogen of the donor end group has the largest local contribution; contributions of opposite signs on the phenylenes and on the acceptor side of the molecule are also significant (we note that the local contributions on the hydrogens are not negligible). Overall, this pattern of β charges, as pointed out earlier, reflects an efficient field-induced nonlinear charge transfer: there occurs a long-range charge transfer between the donor and the acceptor, without any significant cancellation of β moments on neighboring

TABLE I. Transition energy (E_{12}), optical-absorption maximum (λ_{max}), averaged second-order polarizability ($\langle\beta\rangle$), and long-axis component of the second-order polarizability (β_{xxx}) calculated with the SOS and FF methods for compounds 1–14.

Chromophores	E_{12} (eV)	λ_{max} (nm)	$\langle\beta\rangle$ (10^{-30} esu)[a]-SOS	β_{xxx} (10^{-30} esu)-SOS	β_{xxx} (10^{-30} esu)-FF
1	3.04	408	122	131	133
2	2.93	423	166	176	174
3	3.08	403	107	116	117
4	2.62	473	265	275	255
5	2.76	449	206	216	176
6	2.93	423	141	99	83
7	3.02	411	72	68	55
8	3.31	375	56	45	42
9	2.80	443	203	207	218
10	2.86	434	160	165	142
11	2.29	541	506	496	506
12	2.26	549	475	490	514
13	2.12	585	731	730	670
14	2.24	554	598	586	562

[a]$\langle\beta\rangle=\{\beta_x^2+\beta_y^2+\beta_z^2\}^{1/2}$ *with* $\beta_x=\beta_{xxx}+1/3(\beta_{xyy}+\beta_{yxy}+\beta_{yyx})+1/3(\beta_{xzz}+\beta_{zxz}+\beta_{zzx})$.

atoms. An example of an inefficient, self-cancelling β-charge pattern has been discussed previously in terms of local contributions[21] in the case of oligomethineimines.

To analyze the contributions to β in chromophores 1–5 in more detail, it is instructive to compare the β-charge distributions. Note that, although the molecular polarizabilities are determined not by the β charges themselves but by their moments, a direct comparison of the β charges is reasonable here since, for molecules of similar size and shape, the moment arms are practically the same. The variations in the magnitude of the β charges are directly induced by the acceptor end groups, as the sum of the negative and positive β charges over the whole molecule has to be zero. Qualitative differences are clearly seen among the acceptor end groups.

(i) In chromophore 1, the largest β charges are found on the carbon atoms in positions 2 and 4 of the furan ring, while the local contributions on the cyano groups are relatively small; note, however, that the cyano groups in the dicyanovinylene unit of the acceptor end group still give rise to appreciable β moments due to their larger distance from the center of the molecule.
(ii) In chromophore 2, the situation remains qualitatively the same with somewhat larger β charges on the carbon in position 4 of the furan ring, the cyano groups, and the atoms forming CF_3 group.
(iii) Significantly stronger modifications are observed in chromophore 4: the increase in β charges on the two cyano groups is much larger (being even larger for the cyano group in position 3 of the TCP acceptor end group); the most striking changes are, however, observed at the carbonyl group, which provides a much more significant contribution to β than the two methyl groups in 1.
(iv) The large β charges on both carbonyl groups and at the carbon atoms in positions 2 and 5 of chromophore 5 partially account for the still appreciable β_{xxx} obtained for this system.

Overall, the plots in Fig. 2 suggest that position 1 of the heterocycle is the most suitable for further modifications of the acceptor end group to achieve even larger β values.

In systems 6–8 (see Fig. 3), only small parts of the acceptor end groups are active and they are usually relatively far from the end of the molecule [in 6 and 7, the most active segments are the dicyanovinylene unit(s); in 8, the carbonyl groups]. The rest of the acceptor end group is characterized by either very small or, in some cases, even opposite-sign β charges. The main observation in chromophore 8 is that the dicyanovinylene unit hardly makes any contribution; this can be related to the reduced conjugation induced by the strong bending of the saturated part of the ring. In chromophore 9, large local contributions are found only in the furan ring and on the dicyanovinylene unit of the acceptor end group; the rest of the acceptor is again relatively inactive.

In chromophore 10, all β charges are concentrated on the dioxaborine unit. The rest of the acceptor part of the molecule appears to be relatively inactive; therefore, we also calculated β_{xxx} for an analog of chromophore 10 carrying a simple dioxaborine ring as the acceptor (chromophore 10′). It is found that β_{xxx} decreases from 142×10^{-30} esu (chromophore 10′) to 105×10^{-30} esu (chromophore 10′). This β_{xxx} reduction results from two effects: (i) the decrease in the magnitude of the β charges on the atoms forming the dioxaborine unit, and (ii) the loss of the β charges on the part of the acceptor that has been removed; the latter is the most important effect because those atoms are further from the center of the chromophore, thus leading to bigger β moments.

The β value shows a nearly threefold increase in going from chromophore 6 to 9, which is upon addition of a furan ring. The latter can be considered as part of the π bridge and displays alternating β charges. The magnitude of the β charges on the donor and acceptor end groups is similar in 6 and 9; however, there occurs a larger cancellation of the β moments within the π bridge of chromophore 9 because of the alternating β charges. Therefore, the β increase from chromophore 6 to 9 is simply due to an increase of the molecular length of chromophore 9.

B. Impact of auxiliary donors and acceptors

Based on previous studies,[17] it is known that increasing the polyene segment length leads to an increase in β_{xxx} but typically decreases the chromophore thermal and photochemical stabilities. Replacement with phenylenes can increase the overall stability of the chromophores but decreases β_{xxx} significantly due to the resistance of strongly aromatic rings to ground-state polarization. Therefore, the replacement of polyene segments by five-membered heterocycles can offer a good compromise. Since these heterocycles can present high-lying highest occupied molecular orbitals (HOMO's) or low-lying lowest unoccupied molecular orbitals (LUMO's), they can act as secondary donors or acceptors, as has been suggested earlier.[9] To analyze the potential impact of the presence of such auxiliary donors or acceptors, we have studied chromophores 11–14. We have kept the dimethylanilino donor end group and the acceptor end group is taken to be the same as in chromophore 4, which is the most efficient from the series of molecules discussed above.

From Fig. 4, we observe that chromophores 11–14 show fewer alternating β charges and thus less self-cancellation of β moments than in the previous chromophores. The two systems in which an auxiliary acceptor (thiazole) is inserted into the π bridge have higher second-order polarizabilities [$\beta_{xxx}(13)=670\times10^{-30}$ esu and $\beta_{xxx}(14)=562\times10^{-30}$ esu] than when an auxiliary donor (thiophene) is inserted [$\beta_{xxx}(11)=506\times10^{-30}$ esu and $\beta_{xxx}(12)=514\times10^{-30}$ esu]. Interestingly, the location of the thiophene ring has almost no effect, while β_{xxx} is nearly 20% higher when the thiazole is next to the acceptor end group than when it is closer to the donor end group. A conformational origin for these differences can be excluded because the same behavior is observed when the π bridge of the investigated systems is constrained to remain in a fully coplanar conformation.

From the plots in Fig. 4, two factors can be seen to be responsible for the two- to nearly threefold increase of β from 4 to 11–14: (i) the magnitudes of the β charges, in

particular, in the acceptor end group, are much larger in 11–14, and (ii) due to the greater length of the molecules, the corresponding β moments are further increased. Point (i) can, at least partly, be explained by the observation that the β charges on the auxiliary donor and acceptor are mostly negative and relatively large. Invoking the rule that the sum over all β charges of the molecule has to be zero, this paves the way for larger positive β charges on the main acceptor. Comparing the two thiophene-containing systems, very similar β-charge patterns are found, which is consistent with the nearly identical β_{xxx}. In contrast, especially in chromophore 13, both the negative β charges along the π bridge and the positive β charges on the acceptor end group are significantly increased, which gives rise to the very large β in chromophore 13.

IV. CONCLUSIONS

Sum-over-states (SOS) and finite-field (FF) calculations have been carried out in order to predict the molecular second-order polarizability of donor-acceptor substituted dipolar chromophores incorporating a variety of strong heterocyclic acceptor end groups. To obtain a clear picture of the relationship between the magnitude of β and the details of the chemical structure, the local-contributions approach to the FF technique has been applied. The long-axis components of the second-order polarizability (β_{xxx}) calculated with the different approaches are self-consistent and can be expected to reflect the major features of the evolution of the molecular second-order NLO polarizability.

The TCP acceptor end group in chromophore 4 was found to give the highest second-order polarizability among the acceptor end groups we have considered. In general, the TCF and TCP acceptor end groups were found to yield β values superior to many strong acceptor end groups commonly used in NLO chromophores; this can be explained by the fact that in the latter groups, significant parts of the acceptor appear to be relatively inactive in terms of contributing β moments.

When an auxiliary acceptor (thiazole) is inserted into the π bridge of chromophore 4, β increases by a factor of more than 2. This is remarkable since the origin of that increase is not simply found in the increased conjugation length of that system.

In general, the FF method in its local contribution version has allowed us to provide an explanation for why the TCF-based dipolar donor-acceptor chromophores are good candidates for optoelectronics and photonics since the pattern of β charges reflects an efficient field-induced nonlinear charge transfer: it is long range and goes from the donor end to the acceptor end, nearly without cancellation of β moments on neighboring atoms.

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